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# *catena*-Poly[[[{1-[(*E*)-phenyl(pyridin-2-yl-κ*N*)methylidene]semicarbazidato-κ$^2N^1$,*O*}copper(II)]-μ-dicyanamido-κ$^2N^1$:*N*$^5$] monohydrate]

**Roji J. Kunnath,[a] M.R. Prathapachandra Kurup[a] and Seik Weng Ng[b,c]***

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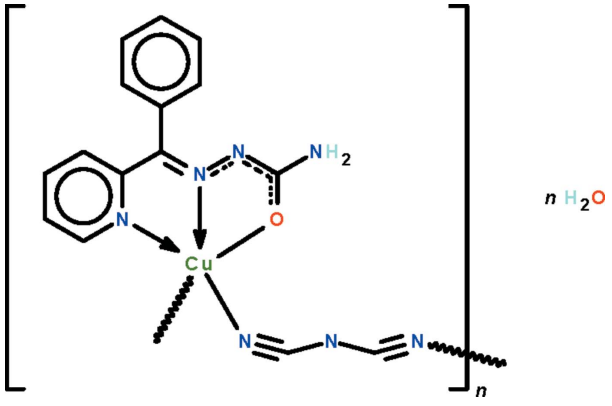
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean σ(C–C) = 0.007 Å; disorder in solvent or counterion; $R$ factor = 0.050; $wR$ factor = 0.166; data-to-parameter ratio = 17.5.

The Cu$^{II}$ atoms in the title coordination polymer, {[Cu($C_{13}H_{11}N_4O$)($C_2N_3$)]·$H_2O$}$_n$, are *N*,*N*′,*O*-chelated by the deprotonated Schiff base ligands, and adjacent metal atoms are bridged by the dicyanamide ions, generating a polymeric chain that propagates along the *b* axis. The two independent metal atoms show a square-pyramidal $N_4O$ coordination. The two independent water molecules are disordered over two positions; each water molecule is a hydrogen-bond donor to a carbonyl O atom. Weak N—H···N hydrogen bonding is also observed.

## Related literature

For the synthesis of the Schiff base ligand, see: de Lima *et al.* (2008). For a related copper(II) derivative, see: Peŕez-Rebolledo *et al.* (2006).




## Experimental

### Crystal data

[Cu($C_{13}H_{11}N_4O$)($C_2N_3$)]·$H_2O$
$M_r$ = 386.86
Orthorhombic, *Pbca*
$a$ = 12.3996 (2) Å
$b$ = 21.0115 (4) Å
$c$ = 26.7059 (5) Å
$V$ = 6957.8 (2) Å$^3$
$Z$ = 16
Mo $K\alpha$ radiation
$\mu$ = 1.28 mm$^{-1}$
$T$ = 293 K
0.40 × 0.30 × 0.20 mm

### Data collection

Bruker Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.629, $T_{max}$ = 0.784
110924 measured reflections
7982 independent reflections
5027 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.166
$S$ = 1.12
7982 reflections
457 parameters
12 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.80 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.46 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H42···N7$^{i}$ | 0.88 | 2.13 | 3.006 (5) | 176 |
| N8—H82···N3$^{ii}$ | 0.88 | 2.15 | 3.025 (5) | 179 |
| O1w—H1w1···O1 | 0.84 | 2.05 | 2.88 (2) | 169 |
| O2w—H2w1···O2 | 0.84 | 2.34 | 3.151 (19) | 161 |

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5601).

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# supporting information

*Acta Cryst.* (2012). E**68**, m1176 [doi:10.1107/S1600536812035283]

## *catena*-Poly[[[{1-[(*E*)-phenyl(pyridin-2-yl-$\kappa N$)methylidene]semicarbazidato-$\kappa^2N^1,O$}copper(II)]-$\mu$-dicyanamido-$\kappa^2N^1:N^5$] monohydrate]

**Roji J. Kunnath, M.R. Prathapachandra Kurup and Seik Weng Ng**

### S1. Comment

2-Benzoylpyridine semicarbazone (de Lima *et al.*, 2008) is a Schiff base that is capable of *N*,*N*′,*O*-chelation to transition metal ions. This feature has been documented a copper(II) dichloride adduct; in this, the Schiff base exists as a neutral molecule (Peŕez-Rebolledo *et al.*, 2006). However, the $Cu^{II}$ atom in the coordination polymer, $[Cu(C_2N_3)(C_{13}H_{11}N_4O)\cdot H_2O]_n$ (I), is *N*,*N*′,*O*-chelated instead by the deprotonated Schiff base (Fig. 1). Adjacent metal atoms are bridged by the dicyanamide ion to generate a chain that propagates along the *b* axis of the orthorhombic unit cell (Fig. 2). The two independent metal atoms show square pyramidal coordination. The two independent water molecules are disordered over two positions; each water molecule is a hydrogen-bond donor to a carbonyl O atom.

### S2. Experimental

A methanol solution (20 ml) of 2-benzoylpyridine semicarbazone (0.240 g,1 mmol) (de Lima *et al.*, 2008), copper acetate monohydrate (0.199 g, 1 mmol) and sodium dicyanamide (0.089 g, 1 mmol) was heated for 5 h. The dark green solid was collected and recrystallized from methanol.

### S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H 0.93 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2*U*(C). The amino H-atoms were similarly treated (N–H 0.88 Å) and their temperature factors tied by a factor of 1.2 times.

Omitted owing interference from the beam stop were (2 1 0), (0 0 2), (1 1 2), (1 1 4) and (1 2 1).

The presence of water was indicated by an infrared spectral measurement. The two independent water molecules are both disordered over two positions; the occupancy could not be refined, and was assumed as a 1:1 type of disorder. For one molecule, the disorder is such that two components are separated by about 2 Å, so that one hydrogen atom should be midway between two oxygen atoms. For the other, the two are separated by about 1 Å, so that one hydrogen atom should be occupying the site of the other oxygen atom. For both, hydrogen atoms were positioned on only one component oxygen atom so that each water molecule forms only one hydrogen bond. Furthermore, the hydrogen atoms were given full occupancy, *i.e.*, hydrogen atoms were not placed on those atoms that do not engage in hydrogen bonding. The temperature factors of the primed atoms were set to those of the unprimed ones, and the anisotropic temperature factors were tightly restrained to be nearly isotropic.

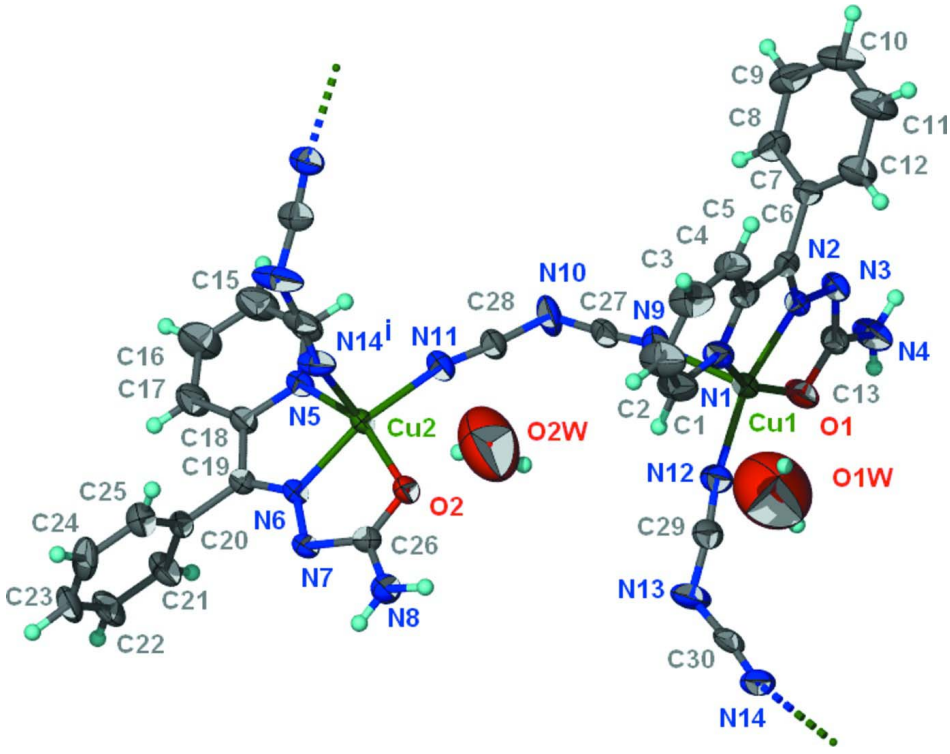


**Figure 1**

Thermal ellipsoid plot (Barbour, 2001) of a portion of the chain structure of $[Cu(C_2N_3)(C_{13}H_{11}N_4O)\cdot H_2O]_n$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The disorder in the water molecules is not shown.

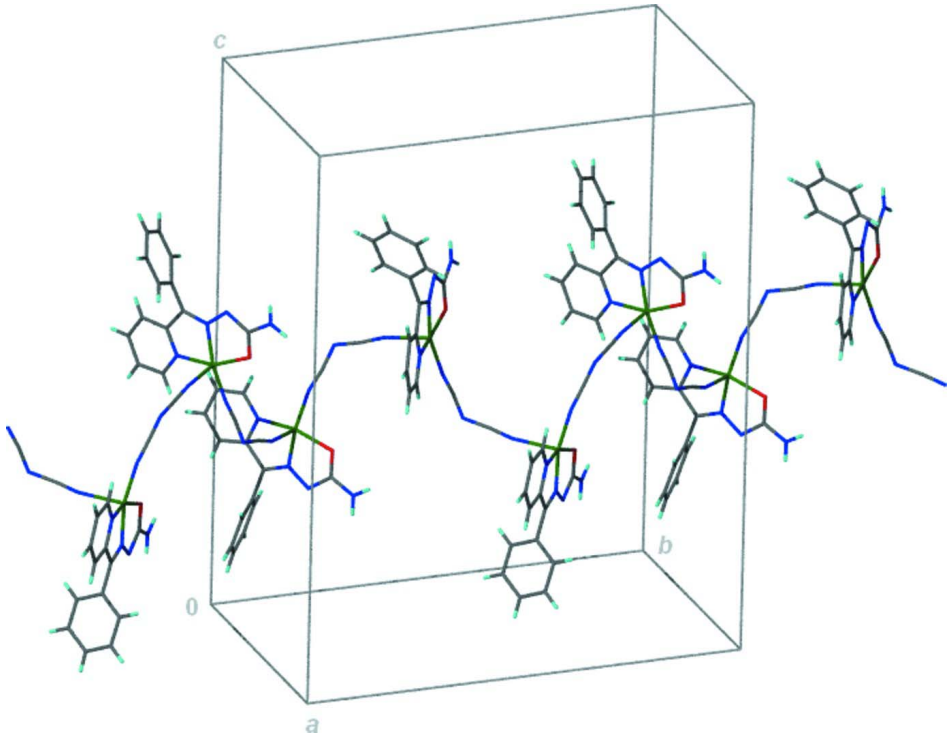


**Figure 2**

Dicyanamide-bridged chain structure. Water molecules are not shown.

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*Crystal data*

$[Cu(C_{13}H_{11}N_4O)(C_2N_3)]\cdot H_2O$
$M_r = 386.86$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 12.3996$ (2) Å
$b = 21.0115$ (4) Å
$c = 26.7059$ (5) Å
$V = 6957.8$ (2) Å$^3$
$Z = 16$
$F(000) = 3152$
$D_x = 1.477$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9967 reflections
$\theta = 2.7$–$26.5°$
$\mu = 1.28$ mm$^{-1}$
$T = 293$ K
Prim, green
0.40 × 0.30 × 0.20 mm

*Data collection*

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.629$, $T_{max} = 0.784$
110924 measured reflections
7982 independent reflections
5027 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$
$h = -16\rightarrow14$
$k = -27\rightarrow27$
$l = -34\rightarrow34$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.166$
$S = 1.12$
7982 reflections
457 parameters
12 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 9.8211P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.80$ e Å$^{-3}$
$\Delta\rho_{min} = -0.46$ e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.74889 (4) | 0.32160 (2) | 0.591725 (16) | 0.03950 (15) | |
| Cu2 | 0.51236 (4) | 0.06952 (2) | 0.406562 (15) | 0.03717 (15) | |
| O1 | 0.6417 (2) | 0.38125 (13) | 0.61888 (10) | 0.0541 (8) | |
| O2 | 0.6166 (2) | 0.13248 (12) | 0.38040 (10) | 0.0489 (7) | |
| O1W | 0.4729 (16) | 0.4332 (10) | 0.5571 (8) | 0.269 (7) | 0.50 |
| H1W1 | 0.5266 | 0.4228 | 0.5745 | 0.404* | |
| H1W2 | 0.4808 | 0.4710 | 0.5475 | 0.404* | |
| O2W | 0.8427 (16) | 0.1463 (9) | 0.4332 (7) | 0.234 (6) | 0.50 |
| H2W1 | 0.7879 | 0.1336 | 0.4177 | 0.280* | |
| H2W2 | 0.8367 | 0.1858 | 0.4373 | 0.280* | |
| O1W′ | 0.4691 (17) | 0.5292 (11) | 0.5296 (8) | 0.269 (7) | 0.50 |
| O2W′ | 0.7929 (19) | 0.1888 (10) | 0.4402 (8) | 0.234 (6) | 0.50 |
| N1 | 0.8834 (3) | 0.26882 (16) | 0.58984 (12) | 0.0469 (8) | |
| N2 | 0.7736 (3) | 0.31179 (14) | 0.66329 (11) | 0.0362 (7) | |
| N3 | 0.7020 (3) | 0.33965 (15) | 0.69487 (11) | 0.0419 (7) | |
| N4 | 0.5629 (3) | 0.41008 (19) | 0.69133 (14) | 0.0644 (11) | |
| H41 | 0.5184 | 0.4351 | 0.6749 | 0.077* | |
| H42 | 0.5586 | 0.4073 | 0.7241 | 0.077* | |
| N5 | 0.3807 (3) | 0.01320 (15) | 0.40768 (10) | 0.0396 (7) | |
| N6 | 0.4882 (2) | 0.06112 (14) | 0.33509 (11) | 0.0358 (7) | |
| N7 | 0.5555 (3) | 0.09307 (15) | 0.30382 (11) | 0.0394 (7) | |
| N8 | 0.6909 (3) | 0.16608 (17) | 0.30793 (13) | 0.0555 (9) | |
| H81 | 0.7353 | 0.1909 | 0.3246 | 0.067* | |
| H82 | 0.6936 | 0.1649 | 0.2750 | 0.067* | |
| N9 | 0.6399 (4) | 0.2399 (2) | 0.58076 (14) | 0.0683 (12) | |
| N10 | 0.5250 (4) | 0.1525 (2) | 0.55530 (14) | 0.0735 (13) | |
| N11 | 0.5158 (3) | 0.09809 (17) | 0.47568 (12) | 0.0497 (8) | |
| N12 | 0.7496 (3) | 0.35269 (18) | 0.52272 (13) | 0.0509 (9) | |
| N13 | 0.7622 (4) | 0.3993 (2) | 0.43995 (14) | 0.0799 (15) | |
| N14 | 0.8717 (3) | 0.48903 (18) | 0.41363 (13) | 0.0539 (9) | |
| C1 | 0.9380 (4) | 0.2496 (2) | 0.54957 (17) | 0.0673 (14) | |
| H1 | 0.9131 | 0.2611 | 0.5180 | 0.081* | |
| C2 | 1.0297 (5) | 0.2132 (3) | 0.5532 (2) | 0.0814 (18) | |
| H2 | 1.0658 | 0.1998 | 0.5246 | 0.098* | |

| | | | | |
|---|---|---|---|---|
| C3 | 1.0669 (5) | 0.1972 (2) | 0.6000 (2) | 0.0747 (16) |
| H3 | 1.1305 | 0.1741 | 0.6035 | 0.090* |
| C4 | 1.0095 (4) | 0.2154 (2) | 0.64189 (17) | 0.0546 (11) |
| H4 | 1.0326 | 0.2039 | 0.6737 | 0.066* |
| C5 | 0.9172 (3) | 0.25110 (17) | 0.63568 (14) | 0.0419 (9) |
| C6 | 0.8486 (3) | 0.27313 (16) | 0.67749 (13) | 0.0360 (8) |
| C7 | 0.8605 (3) | 0.24717 (17) | 0.72905 (13) | 0.0384 (8) |
| C8 | 0.7886 (4) | 0.2016 (2) | 0.74534 (17) | 0.0546 (11) |
| H8 | 0.7321 | 0.1890 | 0.7247 | 0.066* |
| C9 | 0.8002 (5) | 0.1745 (2) | 0.7924 (2) | 0.0696 (14) |
| H9 | 0.7519 | 0.1436 | 0.8032 | 0.084* |
| C10 | 0.8835 (5) | 0.1935 (3) | 0.82286 (19) | 0.0758 (16) |
| H10 | 0.8909 | 0.1758 | 0.8546 | 0.091* |
| C11 | 0.9552 (5) | 0.2379 (3) | 0.80682 (19) | 0.0831 (17) |
| H11 | 1.0119 | 0.2504 | 0.8275 | 0.100* |
| C12 | 0.9440 (4) | 0.2645 (2) | 0.76020 (17) | 0.0653 (13) |
| H12 | 0.9937 | 0.2947 | 0.7494 | 0.078* |
| C13 | 0.6370 (3) | 0.37643 (18) | 0.66655 (14) | 0.0427 (9) |
| C14 | 0.3281 (4) | −0.0096 (2) | 0.44722 (15) | 0.0527 (11) |
| H14 | 0.3484 | 0.0040 | 0.4790 | 0.063* |
| C15 | 0.2455 (4) | −0.0522 (3) | 0.44297 (19) | 0.0741 (16) |
| H15 | 0.2098 | −0.0671 | 0.4713 | 0.089* |
| C16 | 0.2161 (5) | −0.0725 (3) | 0.3959 (2) | 0.0832 (18) |
| H16 | 0.1602 | −0.1016 | 0.3920 | 0.100* |
| C17 | 0.2703 (4) | −0.0494 (2) | 0.35449 (17) | 0.0626 (13) |
| H17 | 0.2513 | −0.0627 | 0.3225 | 0.075* |
| C18 | 0.3520 (3) | −0.00673 (18) | 0.36126 (13) | 0.0403 (8) |
| C19 | 0.4168 (3) | 0.02092 (17) | 0.32052 (13) | 0.0368 (8) |
| C20 | 0.4045 (3) | −0.00038 (17) | 0.26745 (13) | 0.0369 (8) |
| C21 | 0.3209 (4) | 0.0214 (2) | 0.23788 (15) | 0.0562 (11) |
| H21 | 0.2697 | 0.0492 | 0.2508 | 0.067* |
| C22 | 0.3144 (4) | 0.0011 (3) | 0.18867 (17) | 0.0664 (13) |
| H22 | 0.2580 | 0.0154 | 0.1687 | 0.080* |
| C23 | 0.3888 (4) | −0.0392 (2) | 0.16898 (16) | 0.0644 (14) |
| H23 | 0.3844 | −0.0514 | 0.1356 | 0.077* |
| C24 | 0.4709 (4) | −0.0618 (2) | 0.19901 (19) | 0.0647 (14) |
| H24 | 0.5207 | −0.0906 | 0.1862 | 0.078* |
| C25 | 0.4789 (4) | −0.0417 (2) | 0.24776 (17) | 0.0521 (10) |
| H25 | 0.5354 | −0.0562 | 0.2676 | 0.062* |
| C26 | 0.6197 (3) | 0.13029 (17) | 0.33247 (14) | 0.0409 (9) |
| C27 | 0.5897 (4) | 0.1987 (2) | 0.56680 (14) | 0.0471 (10) |
| C28 | 0.5253 (3) | 0.12554 (19) | 0.51235 (14) | 0.0447 (9) |
| C29 | 0.7585 (3) | 0.3768 (2) | 0.48527 (16) | 0.0483 (10) |
| C30 | 0.8225 (3) | 0.4478 (2) | 0.42797 (13) | 0.0455 (10) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0501 (3) | 0.0411 (3) | 0.0272 (2) | −0.00041 (19) | 0.00001 (19) | −0.00053 (18) |
| Cu2 | 0.0476 (3) | 0.0394 (3) | 0.0245 (2) | −0.0023 (2) | −0.00390 (18) | −0.00204 (17) |
| O1 | 0.070 (2) | 0.0597 (18) | 0.0327 (14) | 0.0195 (15) | −0.0050 (13) | 0.0012 (12) |
| O2 | 0.0662 (19) | 0.0471 (16) | 0.0334 (14) | −0.0157 (14) | −0.0080 (13) | −0.0001 (11) |
| O1W | 0.220 (9) | 0.323 (11) | 0.266 (10) | 0.038 (8) | −0.025 (8) | −0.002 (8) |
| O2W | 0.247 (10) | 0.253 (11) | 0.201 (8) | 0.037 (8) | −0.069 (8) | −0.052 (8) |
| O1W′ | 0.220 (9) | 0.323 (11) | 0.266 (10) | 0.038 (8) | −0.025 (8) | −0.002 (8) |
| O2W′ | 0.247 (10) | 0.253 (11) | 0.201 (8) | 0.037 (8) | −0.069 (8) | −0.052 (8) |
| N1 | 0.059 (2) | 0.0457 (18) | 0.0354 (17) | 0.0038 (16) | 0.0107 (15) | 0.0022 (14) |
| N2 | 0.0452 (18) | 0.0354 (16) | 0.0281 (14) | 0.0019 (14) | −0.0007 (13) | −0.0020 (12) |
| N3 | 0.046 (2) | 0.0472 (18) | 0.0323 (16) | 0.0081 (15) | −0.0028 (14) | −0.0045 (14) |
| N4 | 0.075 (3) | 0.078 (3) | 0.0401 (19) | 0.036 (2) | 0.0021 (18) | 0.0022 (18) |
| N5 | 0.0458 (19) | 0.0448 (17) | 0.0282 (15) | −0.0011 (14) | 0.0010 (13) | 0.0004 (13) |
| N6 | 0.0418 (18) | 0.0395 (17) | 0.0261 (14) | −0.0010 (13) | −0.0031 (12) | −0.0002 (12) |
| N7 | 0.0487 (19) | 0.0429 (17) | 0.0266 (14) | −0.0060 (15) | −0.0046 (13) | 0.0028 (13) |
| N8 | 0.070 (3) | 0.054 (2) | 0.0427 (19) | −0.0245 (19) | −0.0014 (17) | 0.0026 (16) |
| N9 | 0.090 (3) | 0.063 (2) | 0.052 (2) | −0.027 (2) | 0.001 (2) | −0.0150 (19) |
| N10 | 0.097 (3) | 0.082 (3) | 0.041 (2) | −0.045 (3) | 0.021 (2) | −0.029 (2) |
| N11 | 0.062 (2) | 0.055 (2) | 0.0321 (17) | −0.0067 (17) | −0.0025 (15) | −0.0054 (15) |
| N12 | 0.058 (2) | 0.056 (2) | 0.0389 (19) | −0.0099 (17) | 0.0001 (16) | 0.0063 (16) |
| N13 | 0.100 (3) | 0.096 (3) | 0.043 (2) | −0.056 (3) | −0.028 (2) | 0.030 (2) |
| N14 | 0.061 (2) | 0.058 (2) | 0.0425 (19) | −0.0145 (19) | −0.0045 (17) | 0.0155 (16) |
| C1 | 0.089 (4) | 0.068 (3) | 0.044 (2) | 0.022 (3) | 0.027 (2) | 0.007 (2) |
| C2 | 0.101 (4) | 0.084 (4) | 0.060 (3) | 0.041 (3) | 0.036 (3) | 0.007 (3) |
| C3 | 0.079 (4) | 0.069 (3) | 0.076 (4) | 0.035 (3) | 0.031 (3) | 0.011 (3) |
| C4 | 0.062 (3) | 0.051 (2) | 0.051 (3) | 0.012 (2) | 0.007 (2) | 0.009 (2) |
| C5 | 0.050 (2) | 0.0348 (19) | 0.041 (2) | 0.0007 (17) | 0.0088 (17) | 0.0028 (15) |
| C6 | 0.043 (2) | 0.0308 (17) | 0.0345 (18) | −0.0025 (16) | 0.0010 (15) | 0.0002 (14) |
| C7 | 0.043 (2) | 0.0394 (19) | 0.0326 (18) | 0.0044 (16) | 0.0035 (16) | 0.0042 (15) |
| C8 | 0.062 (3) | 0.047 (2) | 0.056 (3) | −0.007 (2) | 0.004 (2) | 0.005 (2) |
| C9 | 0.079 (4) | 0.056 (3) | 0.074 (3) | −0.002 (3) | 0.023 (3) | 0.020 (3) |
| C10 | 0.088 (4) | 0.089 (4) | 0.051 (3) | 0.012 (3) | 0.002 (3) | 0.034 (3) |
| C11 | 0.081 (4) | 0.121 (5) | 0.048 (3) | −0.013 (4) | −0.019 (3) | 0.025 (3) |
| C12 | 0.064 (3) | 0.085 (3) | 0.047 (2) | −0.025 (3) | −0.011 (2) | 0.016 (2) |
| C13 | 0.051 (2) | 0.042 (2) | 0.035 (2) | 0.0092 (18) | −0.0012 (17) | −0.0034 (16) |
| C14 | 0.059 (3) | 0.065 (3) | 0.033 (2) | −0.002 (2) | 0.0065 (19) | 0.0007 (18) |
| C15 | 0.066 (3) | 0.106 (4) | 0.051 (3) | −0.023 (3) | 0.011 (2) | 0.014 (3) |
| C16 | 0.071 (4) | 0.118 (5) | 0.061 (3) | −0.043 (3) | −0.003 (3) | 0.013 (3) |
| C17 | 0.064 (3) | 0.082 (3) | 0.042 (2) | −0.032 (3) | −0.006 (2) | 0.003 (2) |
| C18 | 0.042 (2) | 0.048 (2) | 0.0305 (18) | −0.0046 (17) | −0.0027 (15) | −0.0003 (15) |
| C19 | 0.042 (2) | 0.0369 (19) | 0.0314 (18) | −0.0001 (16) | −0.0041 (15) | 0.0008 (14) |
| C20 | 0.042 (2) | 0.0375 (19) | 0.0307 (18) | −0.0070 (16) | −0.0029 (15) | −0.0030 (14) |
| C21 | 0.059 (3) | 0.071 (3) | 0.038 (2) | 0.011 (2) | −0.011 (2) | −0.008 (2) |
| C22 | 0.076 (3) | 0.084 (3) | 0.039 (2) | −0.002 (3) | −0.023 (2) | −0.008 (2) |
| C23 | 0.086 (4) | 0.074 (3) | 0.034 (2) | −0.028 (3) | 0.004 (2) | −0.019 (2) |

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|---|---|---|---|---|---|---|
| C24 | 0.071 (3) | 0.055 (3) | 0.069 (3) | −0.007 (2) | 0.020 (3) | −0.032 (2) |
| C25 | 0.053 (3) | 0.054 (3) | 0.049 (2) | −0.001 (2) | −0.003 (2) | −0.007 (2) |
| C26 | 0.050 (2) | 0.037 (2) | 0.0356 (19) | 0.0002 (17) | −0.0006 (17) | 0.0036 (16) |
| C27 | 0.060 (3) | 0.053 (2) | 0.0280 (18) | −0.007 (2) | 0.0055 (18) | −0.0048 (17) |
| C28 | 0.052 (2) | 0.049 (2) | 0.033 (2) | −0.0117 (19) | 0.0037 (17) | −0.0062 (17) |
| C29 | 0.047 (2) | 0.054 (2) | 0.043 (2) | −0.0148 (19) | −0.0113 (18) | 0.0046 (19) |
| C30 | 0.050 (2) | 0.062 (3) | 0.0252 (18) | −0.008 (2) | −0.0133 (17) | 0.0066 (17) |

*Geometric parameters (Å, º)*

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|---|---|---|---|
| Cu1—N2 | 1.946 (3) | C1—H1 | 0.9300 |
| Cu1—N12 | 1.955 (3) | C2—C3 | 1.376 (7) |
| Cu1—O1 | 1.966 (3) | C2—H2 | 0.9300 |
| Cu1—N1 | 2.004 (4) | C3—C4 | 1.380 (6) |
| Cu1—N9 | 2.205 (4) | C3—H3 | 0.9300 |
| Cu2—N6 | 1.940 (3) | C4—C5 | 1.377 (6) |
| Cu2—N11 | 1.941 (3) | C4—H4 | 0.9300 |
| Cu2—O2 | 1.977 (3) | C5—C6 | 1.479 (5) |
| Cu2—N5 | 2.016 (3) | C6—C7 | 1.488 (5) |
| Cu2—N14$^{i}$ | 2.228 (4) | C7—C8 | 1.378 (6) |
| O1—C13 | 1.278 (4) | C7—C12 | 1.378 (6) |
| O2—C26 | 1.281 (4) | C8—C9 | 1.387 (7) |
| O1W—H1W1 | 0.8401 | C8—H8 | 0.9300 |
| O1W—H1W2 | 0.8401 | C9—C10 | 1.375 (8) |
| O2W—H2W1 | 0.8400 | C9—H9 | 0.9300 |
| O2W—H2W2 | 0.8400 | C10—C11 | 1.359 (8) |
| N1—C1 | 1.333 (5) | C10—H10 | 0.9300 |
| N1—C5 | 1.346 (5) | C11—C12 | 1.371 (6) |
| N2—C6 | 1.292 (5) | C11—H11 | 0.9300 |
| N2—N3 | 1.358 (4) | C12—H12 | 0.9300 |
| N3—C13 | 1.349 (5) | C14—C15 | 1.364 (7) |
| N4—C13 | 1.334 (5) | C14—H14 | 0.9300 |
| N4—H41 | 0.8800 | C15—C16 | 1.377 (7) |
| N4—H42 | 0.8800 | C15—H15 | 0.9300 |
| N5—C14 | 1.331 (5) | C16—C17 | 1.383 (7) |
| N5—C18 | 1.356 (4) | C16—H16 | 0.9300 |
| N6—C19 | 1.284 (5) | C17—C18 | 1.365 (6) |
| N6—N7 | 1.358 (4) | C17—H17 | 0.9300 |
| N7—C26 | 1.353 (5) | C18—C19 | 1.472 (5) |
| N8—C26 | 1.332 (5) | C19—C20 | 1.494 (5) |
| N8—H81 | 0.8800 | C20—C25 | 1.372 (6) |
| N8—H82 | 0.8800 | C20—C21 | 1.381 (6) |
| N9—C27 | 1.129 (5) | C21—C22 | 1.384 (6) |
| N10—C28 | 1.280 (5) | C21—H21 | 0.9300 |
| N10—C27 | 1.296 (6) | C22—C23 | 1.358 (7) |
| N11—C28 | 1.143 (5) | C22—H22 | 0.9300 |
| N12—C29 | 1.127 (5) | C23—C24 | 1.381 (7) |
| N13—C29 | 1.300 (5) | C23—H23 | 0.9300 |

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| N13—C30 | 1.303 (6) | C24—C25 | 1.372 (6) |
| N14—C30 | 1.127 (5) | C24—H24 | 0.9300 |
| N14—Cu2$^{ii}$ | 2.228 (4) | C25—H25 | 0.9300 |
| C1—C2 | 1.372 (7) | | |

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|---|---|---|---|
| N2—Cu1—N12 | 163.76 (14) | N2—C6—C7 | 125.0 (3) |
| N2—Cu1—O1 | 79.14 (12) | C5—C6—C7 | 121.8 (3) |
| N12—Cu1—O1 | 97.91 (14) | C8—C7—C12 | 118.6 (4) |
| N2—Cu1—N1 | 80.51 (13) | C8—C7—C6 | 118.8 (4) |
| N12—Cu1—N1 | 99.07 (14) | C12—C7—C6 | 122.4 (4) |
| O1—Cu1—N1 | 157.69 (13) | C7—C8—C9 | 120.3 (5) |
| N2—Cu1—N9 | 98.30 (14) | C7—C8—H8 | 119.9 |
| N12—Cu1—N9 | 97.91 (15) | C9—C8—H8 | 119.9 |
| O1—Cu1—N9 | 97.52 (15) | C10—C9—C8 | 119.6 (5) |
| N1—Cu1—N9 | 94.37 (16) | C10—C9—H9 | 120.2 |
| N6—Cu2—N11 | 165.22 (14) | C8—C9—H9 | 120.2 |
| N6—Cu2—O2 | 79.29 (12) | C11—C10—C9 | 120.3 (4) |
| N11—Cu2—O2 | 96.58 (13) | C11—C10—H10 | 119.8 |
| N6—Cu2—N5 | 80.58 (12) | C9—C10—H10 | 119.8 |
| N11—Cu2—N5 | 100.68 (13) | C10—C11—C12 | 120.0 (5) |
| O2—Cu2—N5 | 158.01 (11) | C10—C11—H11 | 120.0 |
| N6—Cu2—N14$^{i}$ | 96.54 (13) | C12—C11—H11 | 120.0 |
| N11—Cu2—N14$^{i}$ | 98.04 (14) | C11—C12—C7 | 121.1 (4) |
| O2—Cu2—N14$^{i}$ | 96.66 (13) | C11—C12—H12 | 119.5 |
| N5—Cu2—N14$^{i}$ | 94.34 (14) | C7—C12—H12 | 119.5 |
| C13—O1—Cu1 | 110.4 (2) | O1—C13—N4 | 118.9 (4) |
| C26—O2—Cu2 | 110.4 (2) | O1—C13—N3 | 125.2 (3) |
| H1W1—O1W—H1W2 | 108.7 | N4—C13—N3 | 115.9 (3) |
| H2W1—O2W—H2W2 | 107.9 | N5—C14—C15 | 122.6 (4) |
| C1—N1—C5 | 119.4 (4) | N5—C14—H14 | 118.7 |
| C1—N1—Cu1 | 127.6 (3) | C15—C14—H14 | 118.7 |
| C5—N1—Cu1 | 112.9 (3) | C14—C15—C16 | 118.6 (4) |
| C6—N2—N3 | 124.0 (3) | C14—C15—H15 | 120.7 |
| C6—N2—Cu1 | 117.9 (2) | C16—C15—H15 | 120.7 |
| N3—N2—Cu1 | 117.5 (2) | C15—C16—C17 | 119.5 (5) |
| C13—N3—N2 | 106.8 (3) | C15—C16—H16 | 120.3 |
| C13—N4—H41 | 120.0 | C17—C16—H16 | 120.3 |
| C13—N4—H42 | 120.0 | C18—C17—C16 | 119.1 (4) |
| H41—N4—H42 | 120.0 | C18—C17—H17 | 120.5 |
| C14—N5—C18 | 119.1 (4) | C16—C17—H17 | 120.5 |
| C14—N5—Cu2 | 128.3 (3) | N5—C18—C17 | 121.2 (4) |
| C18—N5—Cu2 | 112.3 (2) | N5—C18—C19 | 114.2 (3) |
| C19—N6—N7 | 124.2 (3) | C17—C18—C19 | 124.5 (3) |
| C19—N6—Cu2 | 117.7 (2) | N6—C19—C18 | 114.3 (3) |
| N7—N6—Cu2 | 117.7 (2) | N6—C19—C20 | 123.7 (3) |
| C26—N7—N6 | 107.4 (3) | C18—C19—C20 | 121.8 (3) |
| C26—N8—H81 | 120.0 | C25—C20—C21 | 119.7 (4) |
| C26—N8—H82 | 120.0 | C25—C20—C19 | 119.0 (3) |

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|---|---|---|---|
| H81—N8—H82 | 120.0 | C21—C20—C19 | 121.4 (3) |
| C27—N9—Cu1 | 168.1 (4) | C20—C21—C22 | 119.0 (4) |
| C28—N10—C27 | 122.9 (4) | C20—C21—H21 | 120.5 |
| C28—N11—Cu2 | 166.7 (3) | C22—C21—H21 | 120.5 |
| C29—N12—Cu1 | 170.9 (4) | C23—C22—C21 | 121.4 (5) |
| C29—N13—C30 | 122.2 (4) | C23—C22—H22 | 119.3 |
| C30—N14—Cu2$^{ii}$ | 164.2 (3) | C21—C22—H22 | 119.3 |
| N1—C1—C2 | 122.2 (5) | C22—C23—C24 | 119.4 (4) |
| N1—C1—H1 | 118.9 | C22—C23—H23 | 120.3 |
| C2—C1—H1 | 118.9 | C24—C23—H23 | 120.3 |
| C1—C2—C3 | 118.5 (4) | C25—C24—C23 | 119.9 (4) |
| C1—C2—H2 | 120.7 | C25—C24—H24 | 120.1 |
| C3—C2—H2 | 120.7 | C23—C24—H24 | 120.1 |
| C2—C3—C4 | 119.7 (5) | C20—C25—C24 | 120.7 (4) |
| C2—C3—H3 | 120.1 | C20—C25—H25 | 119.7 |
| C4—C3—H3 | 120.1 | C24—C25—H25 | 119.7 |
| C5—C4—C3 | 118.8 (4) | O2—C26—N8 | 119.4 (4) |
| C5—C4—H4 | 120.6 | O2—C26—N7 | 124.6 (3) |
| C3—C4—H4 | 120.6 | N8—C26—N7 | 116.0 (3) |
| N1—C5—C4 | 121.2 (4) | N9—C27—N10 | 173.3 (5) |
| N1—C5—C6 | 114.9 (3) | N11—C28—N10 | 172.7 (5) |
| C4—C5—C6 | 123.9 (4) | N12—C29—N13 | 173.4 (5) |
| N2—C6—C5 | 112.9 (3) | N14—C30—N13 | 174.2 (4) |

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| N2—Cu1—O1—C13 | −7.3 (3) | C3—C4—C5—N1 | −0.8 (7) |
| N12—Cu1—O1—C13 | −171.1 (3) | C3—C4—C5—C6 | 179.6 (4) |
| N1—Cu1—O1—C13 | −31.8 (5) | N3—N2—C6—C5 | −178.4 (3) |
| N9—Cu1—O1—C13 | 89.8 (3) | Cu1—N2—C6—C5 | 10.5 (4) |
| N6—Cu2—O2—C26 | −5.6 (3) | N3—N2—C6—C7 | 7.6 (6) |
| N11—Cu2—O2—C26 | −171.2 (3) | Cu1—N2—C6—C7 | −163.6 (3) |
| N5—Cu2—O2—C26 | −29.6 (5) | N1—C5—C6—N2 | −7.2 (5) |
| N14$^{i}$—Cu2—O2—C26 | 89.9 (3) | C4—C5—C6—N2 | 172.5 (4) |
| N2—Cu1—N1—C1 | −178.0 (4) | N1—C5—C6—C7 | 167.1 (3) |
| N12—Cu1—N1—C1 | −14.5 (4) | C4—C5—C6—C7 | −13.2 (6) |
| O1—Cu1—N1—C1 | −153.6 (4) | N2—C6—C7—C8 | 72.8 (5) |
| N9—Cu1—N1—C1 | 84.3 (4) | C5—C6—C7—C8 | −100.8 (5) |
| N2—Cu1—N1—C5 | 3.5 (3) | N2—C6—C7—C12 | −110.7 (5) |
| N12—Cu1—N1—C5 | 167.1 (3) | C5—C6—C7—C12 | 75.7 (5) |
| O1—Cu1—N1—C5 | 28.0 (5) | C12—C7—C8—C9 | 0.6 (7) |
| N9—Cu1—N1—C5 | −94.2 (3) | C6—C7—C8—C9 | 177.3 (4) |
| N12—Cu1—N2—C6 | −98.0 (5) | C7—C8—C9—C10 | 0.3 (7) |
| O1—Cu1—N2—C6 | −178.9 (3) | C8—C9—C10—C11 | −0.9 (9) |
| N1—Cu1—N2—C6 | −8.1 (3) | C9—C10—C11—C12 | 0.6 (9) |
| N9—Cu1—N2—C6 | 84.9 (3) | C10—C11—C12—C7 | 0.4 (9) |
| N12—Cu1—N2—N3 | 90.3 (6) | C8—C7—C12—C11 | −1.0 (8) |
| O1—Cu1—N2—N3 | 9.4 (3) | C6—C7—C12—C11 | −177.5 (5) |
| N1—Cu1—N2—N3 | −179.8 (3) | Cu1—O1—C13—N4 | −175.2 (3) |
| N9—Cu1—N2—N3 | −86.8 (3) | Cu1—O1—C13—N3 | 5.1 (5) |

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| C6—N2—N3—C13 | 180.0 (3) | N2—N3—C13—O1 | 2.2 (5) |
| Cu1—N2—N3—C13 | −8.9 (4) | N2—N3—C13—N4 | −177.5 (4) |
| N6—Cu2—N5—C14 | −179.3 (4) | C18—N5—C14—C15 | −0.4 (7) |
| N11—Cu2—N5—C14 | −14.2 (4) | Cu2—N5—C14—C15 | −173.8 (4) |
| O2—Cu2—N5—C14 | −155.3 (3) | N5—C14—C15—C16 | 0.4 (9) |
| N14$^{i}$—Cu2—N5—C14 | 84.8 (4) | C14—C15—C16—C17 | −0.2 (10) |
| N6—Cu2—N5—C18 | 6.9 (3) | C15—C16—C17—C18 | 0.0 (9) |
| N11—Cu2—N5—C18 | 172.0 (3) | C14—N5—C18—C17 | 0.2 (6) |
| O2—Cu2—N5—C18 | 30.9 (5) | Cu2—N5—C18—C17 | 174.7 (4) |
| N14$^{i}$—Cu2—N5—C18 | −89.0 (3) | C14—N5—C18—C19 | −179.1 (4) |
| N11—Cu2—N6—C19 | −104.8 (6) | Cu2—N5—C18—C19 | −4.7 (4) |
| O2—Cu2—N6—C19 | −179.8 (3) | C16—C17—C18—N5 | 0.0 (8) |
| N5—Cu2—N6—C19 | −8.7 (3) | C16—C17—C18—C19 | 179.2 (5) |
| N14$^{i}$—Cu2—N6—C19 | 84.7 (3) | N7—N6—C19—C18 | −178.9 (3) |
| N11—Cu2—N6—N7 | 82.0 (6) | Cu2—N6—C19—C18 | 8.4 (4) |
| O2—Cu2—N6—N7 | 7.0 (2) | N7—N6—C19—C20 | 5.5 (6) |
| N5—Cu2—N6—N7 | 178.1 (3) | Cu2—N6—C19—C20 | −167.3 (3) |
| N14$^{i}$—Cu2—N6—N7 | −88.5 (3) | N5—C18—C19—N6 | −2.1 (5) |
| C19—N6—N7—C26 | −179.3 (3) | C17—C18—C19—N6 | 178.6 (4) |
| Cu2—N6—N7—C26 | −6.6 (4) | N5—C18—C19—C20 | 173.7 (3) |
| N2—Cu1—N9—C27 | −157 (2) | C17—C18—C19—C20 | −5.7 (6) |
| N12—Cu1—N9—C27 | 24 (2) | N6—C19—C20—C25 | 74.0 (5) |
| O1—Cu1—N9—C27 | 123 (2) | C18—C19—C20—C25 | −101.3 (4) |
| N1—Cu1—N9—C27 | −76 (2) | N6—C19—C20—C21 | −105.0 (5) |
| N6—Cu2—N11—C28 | −52.0 (19) | C18—C19—C20—C21 | 79.7 (5) |
| O2—Cu2—N11—C28 | 20.8 (16) | C25—C20—C21—C22 | −0.3 (7) |
| N5—Cu2—N11—C28 | −145.5 (16) | C19—C20—C21—C22 | 178.7 (4) |
| N14$^{i}$—Cu2—N11—C28 | 118.5 (16) | C20—C21—C22—C23 | −0.5 (8) |
| C5—N1—C1—C2 | −1.6 (8) | C21—C22—C23—C24 | 1.8 (8) |
| Cu1—N1—C1—C2 | −179.9 (4) | C22—C23—C24—C25 | −2.3 (7) |
| N1—C1—C2—C3 | −1.0 (9) | C21—C20—C25—C24 | −0.3 (6) |
| C1—C2—C3—C4 | 2.7 (9) | C19—C20—C25—C24 | −179.3 (4) |
| C2—C3—C4—C5 | −1.8 (8) | C23—C24—C25—C20 | 1.6 (7) |
| C1—N1—C5—C4 | 2.5 (6) | Cu2—O2—C26—N8 | −175.3 (3) |
| Cu1—N1—C5—C4 | −179.0 (3) | Cu2—O2—C26—N7 | 4.0 (5) |
| C1—N1—C5—C6 | −177.8 (4) | N6—N7—C26—O2 | 1.5 (5) |
| Cu1—N1—C5—C6 | 0.7 (4) | N6—N7—C26—N8 | −179.2 (3) |

Symmetry codes: (i) −*x*+3/2, *y*−1/2, *z*; (ii) −*x*+3/2, *y*+1/2, *z*.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H42···N7$^{iii}$ | 0.88 | 2.13 | 3.006 (5) | 176 |
| N8—H82···N3$^{iv}$ | 0.88 | 2.15 | 3.025 (5) | 179 |
| O1w—H1w1···O1 | 0.84 | 2.05 | 2.88 (2) | 169 |
| O2w—H2w1···O2 | 0.84 | 2.34 | 3.151 (19) | 161 |

Symmetry codes: (iii) *x*, −*y*+1/2, *z*+1/2; (iv) *x*, −*y*+1/2, *z*−1/2.